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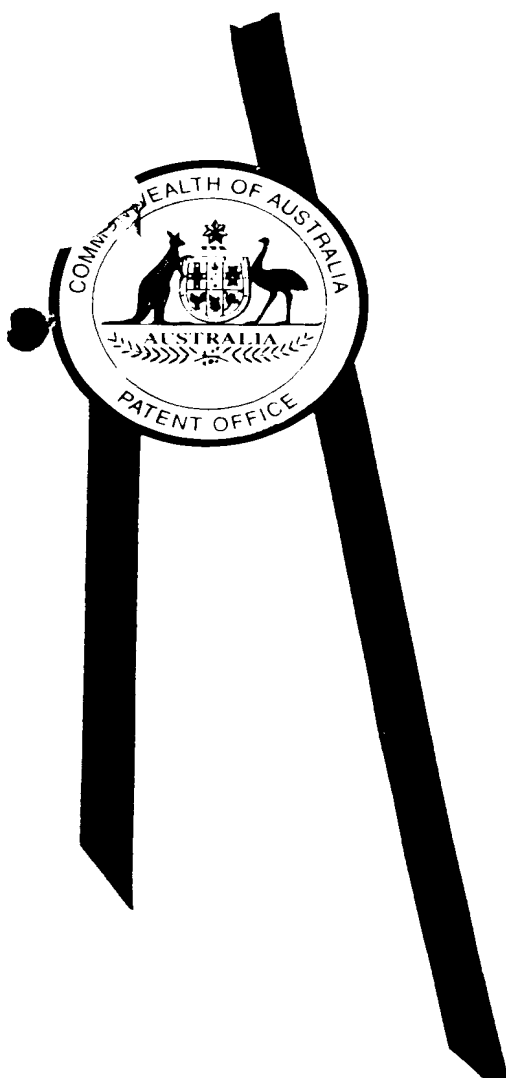
I, CASSANDRA RICHARDS, ACTING TEAM LEADER EXAMINATION SUPPORT & SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. PQ 3264 for a patent by COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION filed on 05 October 1999.

WITNESS my hand this
Third day of November 2000

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AUSTRALIA
Patents Act 1990

PROVISIONAL SPECIFICATION

Applicant(s) :

COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH
ORGANISATION

Invention Title:

NANOPARTICLE FILMS

The invention is described in the following statement:

NANOPARTICLE FILMS

Field of the Invention

The present invention relates broadly to supported nanoparticle films, devices comprising such films and a method of forming such films.

Background of the Invention

Nanoparticles (sometimes also referred to as colloids) are particles of a material which have a dimension of less than typically 1 micrometer. More recently, nanoparticles with dimensions of the order of 10 nm have been investigated in detail, and interesting properties such as large optical polarisability, non-linear electrical conductance, coulomb blockade and coulomb staircase phenomena in the conductance have been revealed. Those investigations have been conducted on substantially single nanoparticles, primarily driven by efforts to utilise single nanoparticles in for example "single electron" electrical devices such as transistors or as "building blocks" for design of molecular devices.

On the other hand, the formation of supported nanoparticle films has been investigated less intensely, which can mainly be attributed to the difficulties of preparing suitable, substantially continuous three-dimensional nanoparticle films. Different methods of forming nanoparticle films have been used, including a sequence of immersions of a substrate in solutions containing the charged nanoparticles and an organic, bifunctional cross-linker respectively. However, this method requires between 2 to 24 hours for each nanoparticle layer to be "deposited". It therefore is doubtful that this method has technological utility.

Filtration of particles from a solution is an established process and in general after filtration one is left with a filter "cake" left on the filtration medium.

When applied to nanoparticles, it is known that this filter cake is subject to cracking on drying especially

when ceramic or ceramic precursors such as silicon dioxide are used. Also, in general, the process of filtration leads to a filter "cake" that is readily redispersable in a liquid. Addition of polymeric binding agents to ceramic
5 powders can be used in certain circumstances to reduce the cracking of the filter "cake" on drying.

However, the "cake" needs to be subjected to high temperature firing for sintering, in order to end up with a film that is not readily redispersable. The sintering on
10 the other hand results in the formation of direct links between the nanoparticles of the "cake" which, although no melting occurs, can mean that some or all of the individual nanoparticle properties are changed.

Conductive and semi-conductive nanoparticles have a
15 tendency to sinter on close contact even at room temperature conditions and therefore it is generally not possible to filter unprotected metal, conductive nanoparticles and semiconducting nanoparticles without the possibility of sintering occurring in the resultant cake.
20 This sintering has been shown to change the opto-electronic properties of the nanoparticles which is undesirable in many applications.

The sintering can be prevented through the use of organic mono- or bifunctional binding agents. These binding
25 agents form relatively strong binding interactions with the nanoparticles and prevent the close contact of the cores of adjoining conducting or semi-conducting nanoparticles. The use of such binding agents leads to the formation of aggregates, either through cross-linking and precipitation
30 or through precipitation of the nanoparticle aggregates due to the insolubility of the coated nanoparticle.

Such nanoparticle aggregates are isolated by addition of a binding agent, allowing the reaction between the binding agent and the nanoparticle to proceed to
35 completion, precipitation and isolation of the precipitate by the use of centrifugation or through the use of

filtration. The filter "cake" formed by this method is readily redispersable and the nanoparticle aggregates can be readily isolated as a bulk material.

5 The filter "cake" formed does not form a nanoparticle thin film array that is adherent on the support and is non-dispersable / non-redissolvable.

Summary of the invention

10 In accordance with a first aspect of the present invention there is provided a method of forming a supported nanoparticle film, the method comprising the steps of preparing a solution containing nanoparticles; adding soluble linker molecules to the solution to start a cross-linking reaction during which the linker molecules form cross-links between the nanoparticles, and filtering the
15 organic solution through a porous support, wherein the filtering step is conducted before the cross-linking reaction has gone to completion.

It has been found that by carrying out the filtration of nanoparticles in the presence of a cross-linking
20 molecule during the period of time before the cross-linking reaction has gone to completion it is possible to form a nanoparticle thin film array that is adherent on the support, is non-dispersable/redissolvable and retains the integrity of the individual nanoparticles.

25 The pore size of the resultant supported nanoparticle film may be adjusted through the use of different size nanoparticles. The pore size being produced by the void space left between the approximately spherical or irregular shaped nanoparticles.

30 It is further preferred that the average pore size is less than 10 nm in diameter.

It has further been determined that it is possible to incorporate an adjustable property within the structure of the thin film or nanoparticle array thus
35 formed.

In accordance with a second aspect of the present invention there is provided a supported nanoparticle film having an adjustable property, being adjustable under the influence of an external stimulus.

5 For the purpose of this specification, such films will also be referred to as "active" films.

In a preferred embodiment the nanoparticles are conducting or semiconducting nanoparticles.

The adjustable property of the nanoparticle film may
10 be its electrical conductivity.

The adjustable property of the nanoparticle film may be its pore size.

The adjustable property of the nanoparticle film may be adjusted by adjusting a property of at least some of
15 linker molecules linking nanoparticles of the nanoparticle film and/or by adjusting a property of at least some of the nanoparticles.

It is further preferred that the pore size is adjusted through the modification of the cross-linking groups.

20 The adjustable property of at least some of the linker molecules may be, but is not limited to, by means of an electroactive group, a reduction/oxidation active group, a pH sensitive group, light responsive group, a protein, an enzyme, a group capable of forming a complex with another
25 molecule, a magnetic responsive group, an electric field responsive group, a group capable of changing its conformation or electronic or optical properties through the application of the external stimulus.

The adjustable property - group may be either an
30 electron donor or electron acceptor group such as a viologen, ferrocene, fullerene, carbon nanotube, aromatic amine compound, aromatic nitro compound, TCNQ.

The adjustable property of at least some of the linker molecules may be such that on application of the external
35 stimulus the conformation of the linker molecule changes in such a way that the interparticle distance between the

nanoparticles is modulated. This has the effect of changing the energetics of the barrier to interparticle electron hopping between nanoparticles resulting in a change in nanoparticle film conductivity.

5 In accordance with a third aspect of the present invention there is provided a device comprising a supported nanoparticle film having an adjustable property.

The device may comprise a multilayer structure of nanoparticle films produced on top of each other.

10 The multilayer structure may comprise two or more nanoparticle film layers wherein at least one nanoparticle film layer contains nanoparticles or cross-linking molecules that are different from those found in the other layer.

15 The multilayer structure may comprise a nanoparticle layer that is cross-linked using a first linker molecule that comprises an electron acceptor molecule and another nanoparticle layer that is cross-linked using a second linker molecule that comprises an electron donor molecule
20 such that electrons flow in one direction of the multilayer structure preferentially to the other direction.

In one embodiment, the device comprises a diode type structure using multilayers with asymmetric electron donor/acceptor properties.

25 In accordance with a fourth aspect of the present invention there is provided a method of forming a supported nanoparticle film, the method comprising the steps of preparing a solution of nanoparticles; adding soluble nanoparticle-linker molecules, said nanoparticle-linker
30 molecules being able to cross-link the nanoparticles and being cross-linkable to each other on application of an external stimulus; allowing the nanoparticles to cross-link due to the action of the nanoparticle-linker molecule, filtering the solution through a porous support, and
35 applying the external stimulus such that the nanoparticle-

linker molecules additionally form cross-links between each other.

The application of the external stimulus may stimulate a polymerisation reaction of the nanoparticle-linker molecules.

Preferred forms of the invention will now be described, by way of example only, with reference to the accompanying drawings, in which:

Brief Description of the Drawings

Figure 1 shows conductivity measurements of different supported nanoparticle films embodying the present invention.

Figure 2 shows a measurement of the changes in conductivity of an "active" nanoparticle film embodying the present invention.

Figure 3 shows current-voltage curves of a device embodying the present invention.

Figure 4 is a schematic drawing of a device embodying the present invention.

Detailed Description of the Preferred Embodiments

The gold nanoparticles used were produced using known nanoparticle formation procedures, which are outlined below:

Gold chloride and trisodiumcitrate are added in water, which is subsequently boiled for 15 minutes. This process results in gold nanoparticles having dimensions of about 5 to 50 nm in aqueous solution.

Alternatively, gold chloride and tetraoctylammonium bromide is added in toluene, a reducing agent is added and the mixture is stirred for 2 hours. This results in gold nanoparticles having dimensions of about 8 nm in organic solution.

In a first embodiment, an organic soluble linker molecule is added to the organic solution containing the gold nanoparticles. Before the reaction has gone to completion in the cross-linking reaction between the gold

nanoparticles and the organic soluble linker molecules, the mixture is then filtered through an Anopore porous support (pore size 20 nm).

The resultant nanoparticle films supported on the Anopore support were found to be coherent and were not readily redispersable/redissolvable.

The Applicant has found that if the cross-linking reaction is allowed to go to completion, a flocculate precipitate is formed. This flocculate precipitate may be filtered through the porous support, but it is not possible to obtain a coherent film. Rather, the flocculate precipitate can be readily redispersed/redissolved from the support.

Further embodiments are now described:

- Formation of Au nanoparticle film on Anopore support (pore size 20nm).

Alkanedithiol is added to an organic solution containing the Au nanoparticles. Before the reaction has gone to completion the mixture is filtered through the Anopore support to form a coherent, supported Au nanoparticle film. Formation of Au nanoparticle film on cellulose acetate/nitrate support.

Alkanedithiol is added to an organic solution containing the Au nanoparticles. Before the reaction has gone to completion the mixture is filtered through the on cellulose acetate/nitrate support to form a coherent, supported Au nanoparticle film.

- Formation of Au nanoparticle film on Durapore support. Alkanedithiol is added to the organic solution containing the Au nanoparticles. Before the reaction has gone to completion the mixture is filtered through the a Durapore support to form a coherent, supported Au nanoparticle film.

- Formation of Au nanoparticle array on Anopore support using different cross-linker lengths

Dithiol cross-linker is added to the organic solution containing the Au nanoparticles. Before the reaction has gone to completion the mixture is filtered through the Anopore support to form a coherent, supported Au nanoparticle film. Varying the length of the dithiol resulted in different conductivities (lateral) of the resultant films. As shown in Figure 1, the conductivity decreases from $1/(100\Omega)$ (2 carbon linker, data points A) to $(1/100\text{ M}\Omega)$ (15 carbon linker, data points C). Similar results can be obtained using diamine cross-linker molecules of varying lengths when gold nanoparticles formed in organic solution as described above are used.

The result that by varying the length of the linker group, by for example using 1,8-octanedithiol and 1,15-pentadecanedithiol the conductivity of the film can be varied, indicates that the gold nanoparticles had not sintered during film formation.

- Formation of Au nanoparticle array on cellulose acetate/nitrate support using viologen cross-linker molecules to form a photoswitched nanoparticle film. Methyl viologen dichloride is added to the aqueous solution containing the Au nanoparticles formed by citrate reduction. Before the reaction has gone to completion the mixture is filtered through the on cellulose acetate/nitrate support to form a coherent, supported Au nanoparticle film.

The resultant nanoparticle film has an adjustable conductivity, adjustably by e.g. exposing the nanoparticle film to radiation from a xenon lamp. Figure 2 shows a measurement of the changes in the (lateral) conductivity of the nanoparticle film during on and off cycles of the xenon lamp.

- Formation of Active Au nanoparticle multilayer array on cellulose acetate/nitrate support.

A patterned, conductive gold nanoparticle film was formed by masking off a circular section of the cellulose acetate/nitrate filter support, followed by filtration of a solution of aqueous Au nanoparticles formed by citrate reduction method, to which had been added a solution of a two carbon linker, cystamine hydrochloride as described above. The mixture was filtered before the reaction between the Au particles and the cystamine cross-linker had gone to completion. The film thus formed was washed with water. A solution of aqueous Au nanoparticles formed by the citrate reduction method, to which had been added a solution of bis(10-decanethiol)-viologen was then filtered through the filter before the reaction had gone to completion. A third film consisting in a solution of aqueous Au nanoparticles formed by citrate reduction method, to which had been added a solution of a two carbon linker, cystamine hydrochloride was formed on top of the previous films by filtration before the reaction had gone to completion. Thus a trilayer film was formed consisting of a bis(10-decanethiol)viologen linked gold nanoparticle array sandwiched between two conductive gold nanoparticle films formed from cystamine hydrochloride linked gold nanoparticle arrays. Current-voltage curves of the device showed non-linear characteristics that may be of utility in electronic applications, as shown in Figure 3.

- Formation of patterned Au nanoparticle film on cellulose acetate/nitrate support using patterned microchannel mask.

A mask is produced from a suitable material such as silicone rubber which through known methods such as casting a mould onto a photolithographed master contains a series of channels and patterns as desired (Kim, E. et al, J. Am. Chem. Soc., 1996, 118, pg 5722-5731). The mask is placed onto the filtration membrane. A solution of Au nanoparticles to which has been added a cross-linker is prepared and used before the cross-linking reaction has

gone to completion. The nanoparticle/cross-linker mixture is allowed to flow through the mask and through those parts of the porous support to which the channels of the mask direct the solution using either pressure or application of vacuum. The material of the mask is such that it is inert to the various solvents used.

- Formation of transistor like devices

A device 10 comprises a number of nanoparticle layers as shown schematically in Figure 4. On a porous support 12 a patterned layer of a conductive nanoparticle film has a source portion 14 and a drain portion 16 of the device 10. A conductive layer of nanoparticles 18 is considered the Gate and an electroactive nanoparticle film 20 whose conductivity may be modulated through the use of an electro/magnetic stimulus encapsulates the source and drain portions 14, 16 respectively.

An insulating layer of nanoparticles 22 is formed between the gate-layer of nanoparticles 18 and the electroactive nanoparticle film 20.

By applying a stimulus at the gate-layer of nanoparticles 18, a flow of current from the source portion 14 to the drain portion 16 can be modulated.

In a further embodiment a solution of gold nanoparticles formed in water using the sodium citrate reduction method was treated with a water soluble cross-linking molecule. Before the reaction between the gold nanoparticles and the cross-linking molecules had gone to completion the mixture was filtered under vacuum or pressure in order to obtain a coherent nanoparticle film.

It was found that if the interaction between the cross-linker groups and the nanoparticles was weak, such as for the case when water soluble diamine compounds were used in an aqueous environment, the resultant nanoparticle films sintered and no relationship between the length of the linker and the conductivity of the nanoparticle film was found. However, when a watersoluble dithiol cross-liner was

used such as bis(10-decanethiol)-viologen, which can form relatively strong gold-sulfur bonds, a highly resistive nanoparticle film was found indicating that the nanoparticles had not sintered.

5 Applications of active nanoparticle films:

- electrically switched filtration membranes, where the filtration of molecules through the pores formed in the nanoparticle film is controlled through application of electric charge onto the conducting membrane.

10 - formation of transistors, PROM devices which utilise nanoparticle films with adjustable photoconductivity or electrical conductivity.

- Electric components such as an antenna which can be "switched" into a non-conductive state when not in
15 operation, to e.g. avoid detection.

- A photovoltaic device formed by the process describe in the invention utilising a multilayer structure of conducting and semiconducting nanoparticles

- Optoelectronic devices wherein the resistors,
20 capacitors, diodes and transistors are formed onto porous supports using multilayers of patterned cross-linked nanoparticle films formed by the filtration method as described above.

It will be appreciated by a person skilled in the art
25 that numerous variations and/or modifications may be made to the present invention as shown in the specific embodiments without departing from the spirit or scope of the invention as broadly described. The present embodiments are, therefore, to be considered in all
30 respects to be illustrative and not restrictive.

The claims defining the invention are

1. A method of forming a supported nanoparticle film,
the method comprising the steps of:
 - preparing a solution containing nanoparticles;
 - 5 - adding soluble linker molecules to the solution to
start a cross-linking reaction during which the linker
molecules form cross-links between the nanoparticles; and
 - filtering the organic solution through a porous
support, wherein the filtering step is conducted before the
10 cross-linking reaction has gone to completion.
2. A supported nanoparticle film having an adjustable
property.
3. A device comprising a supported nanoparticle film
having an adjustable property.
- 15 4. A method of forming a supported nanoparticle film,
the method comprising the steps of:
 - preparing a solution of nanoparticles;
 - adding soluble nanoparticle-linker molecules, said
nanoparticle-linker molecules being able to cross-link the
20 nanoparticles and being cross-linkable to each other on
application of an external stimulus;
 - allowing the nanoparticles to cross-link due to the
action of the nanoparticle-linker molecule;
 - filtering the solution through a porous support; and
 - 25 - applying the external stimulus such that the
nanoparticle-linker molecules additionally form cross-links
between each other.

Dated this 5th day of October 1999

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CSIRO

By their Patent Attorneys

GRIFFITH HACK

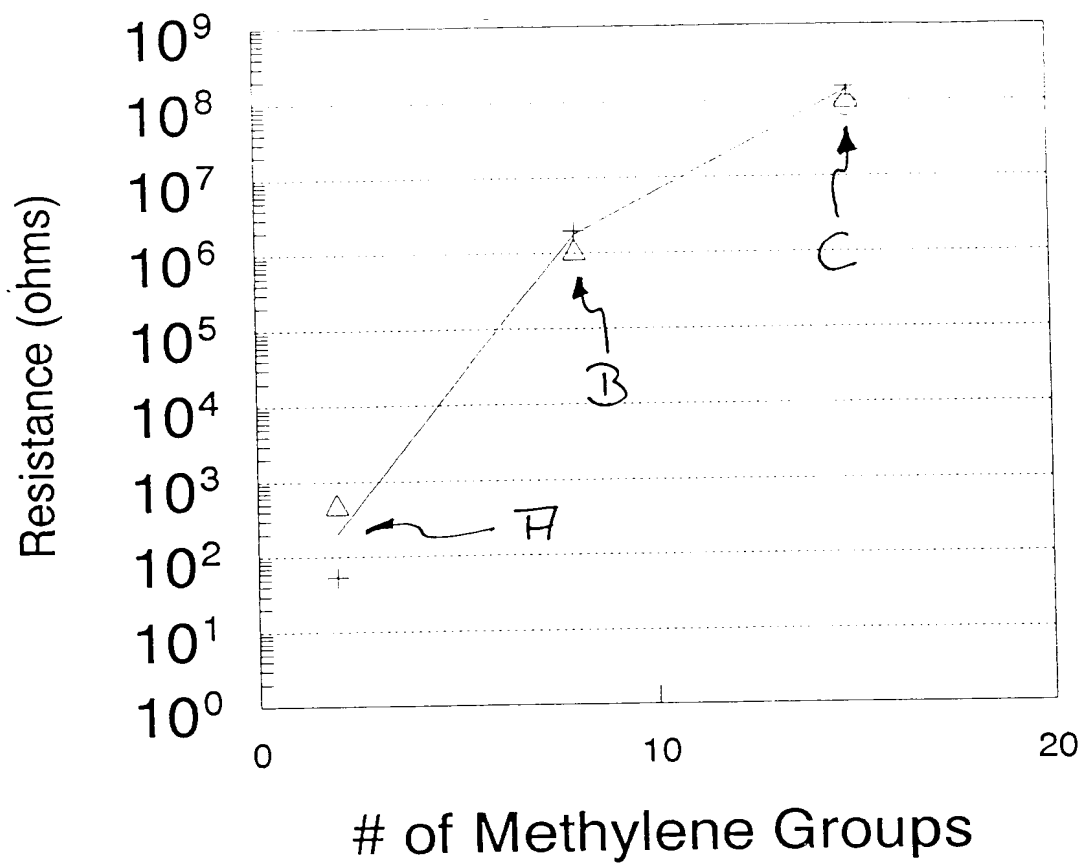


Figure 1

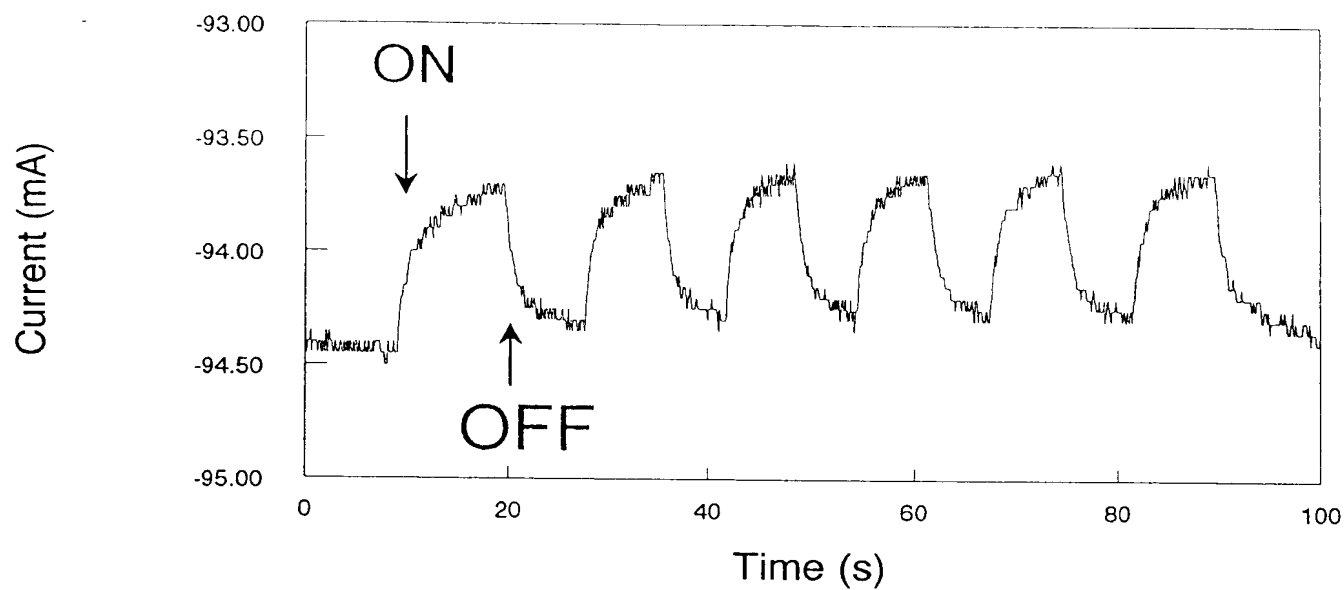


Figure 2

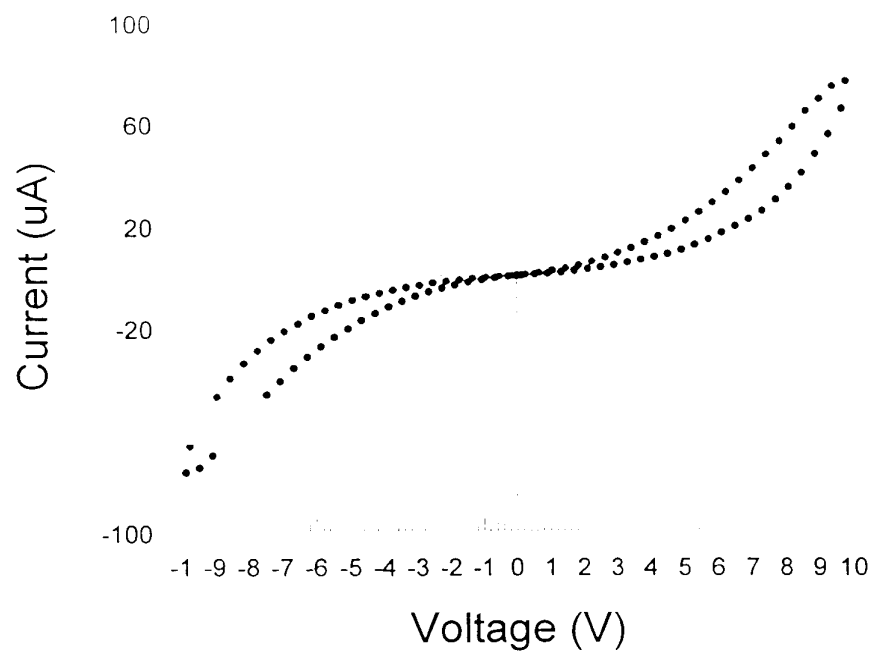


Figure 3

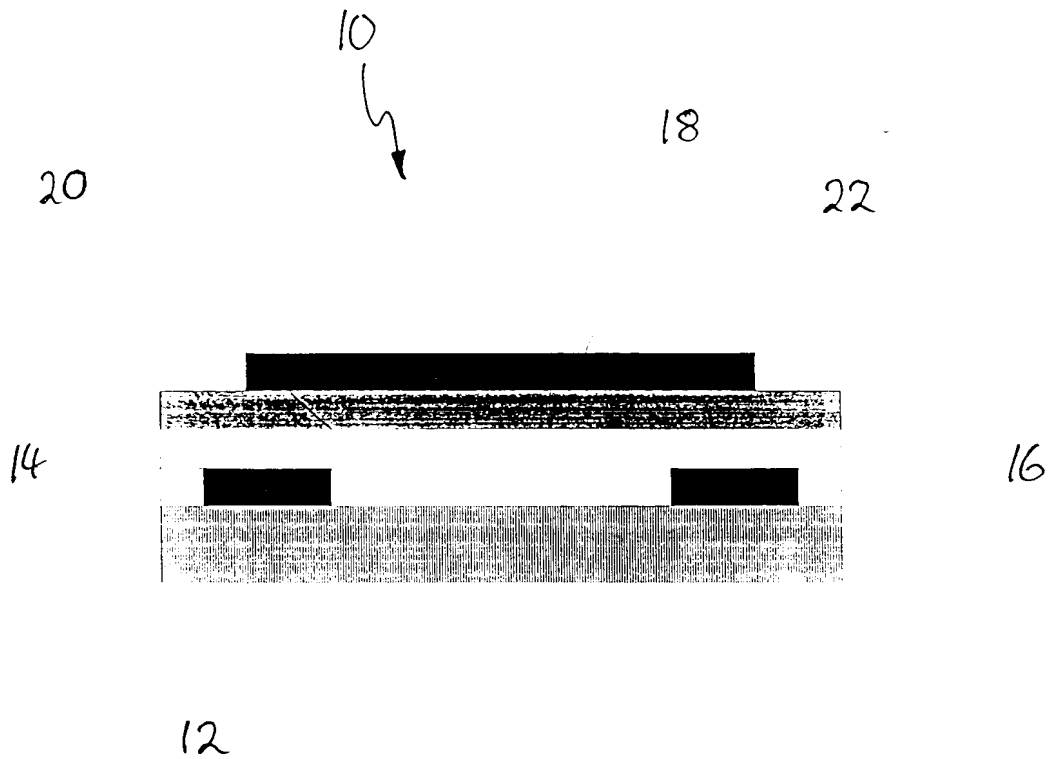


Figure 4